

FREEZING POINT DEPRESSION IN LF_2 SYSTEMS

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In some test programs at Douglas using liquid fluorine and liquid hydrogen, we found it was desirable to lower the freezing point of fluorine without appreciably affecting its chemical reactivity. The use of a eutectic mixture with another cryogenic oxidizer seemed the method of choice, and consideration of physical and chemical properties led us to select oxygen difluoride, OF_2 , for the other component. Oxygen was also suggested, but was not used because of reports of the quenching effect oxygen has on the fluorine-hydrogen reaction (Reference 1), an effect we also found in our research on the ignition of the $\text{LF}_2\text{-LH}_2$ reaction in LH_2 (Reference 2) and which has also been reported in the $\text{OF}_2\text{-H}_2$ reaction (Reference 3). LO_2 was therefore dropped from further consideration.

Theoretical calculations of the freezing point depression in the $\text{F}_2\text{-OF}_2$ system were carried out. These suggested that experimental investigation was warranted.

THEORETICAL

The equilibrium or phase diagram of a two-component solid-liquid system may assume several general forms according to the nature of the components (Reference 4); these forms may be classified as follows:

1. Eutectic Systems
 - a. Simple eutectic
 - b. Monotectic (special form of simple eutectic)
 - c. Compound formation with congruent melting point
 - d. Compound formation with incongruent melting point
2. Completely Miscible Solid Solutions
 - a. Continuous solid solution
 - b. Minimum melting solid solution
 - c. Maximum melting solid solution
3. Partially Miscible Solid Solutions
 - a. Peritectic solid solution
 - b. Eutectic solid solution

In order for nonpolar compounds to form solid solutions, the following conditions must generally be satisfied:

1. Analogous chemical constitutions
2. Similar crystal structures
3. Nearly equal molecular volumes

While little is known of the crystal structures of F_2 and OF_2 , it is certain that conditions 1 and 3 are not satisfied, and it is unlikely that solid solutions will form. Furthermore, there is no known tendency toward compound formation between OF_2 and F_2 . Thus simple eutectic or monotectic systems are probable -- and the latter are rarely encountered.

If it is assumed that the system would be a simple eutectic, with the solution of each component in the other obeying Raoult's Law, and the liquidus curves conforming to equations for ideal solutions, the following considerations will apply:

From the Clausius-Clapeyron equation it can be shown that for equilibrium between solid solvent and vapor, at constant pressure,

$$\frac{d \ln P_s}{dT} = \frac{L_s}{RT^2}$$

For an equilibrium between liquid and vapor, the corresponding equation is

$$\frac{d \ln P_L}{dT} = \frac{L_e}{RT^2}$$

If it is assumed that the equations hold for supercooled solution in contact with solid, then

$$\frac{d \ln(P_s/P_L)}{dT} = \frac{L_s - L_e}{RT^2} = \frac{L_f}{RT^2}$$

At the freezing point of the solution, the vapor pressure of the solid solvent must equal that of the solution, hence

$$\frac{d \ln(P_1/P_L)}{dT} = \frac{L_f}{RT^2}$$

Since $P_1/P_L = X_1$ (mole fraction of solvent in solution) if Raoult's Law is applicable, then

$$\frac{d \ln X_1}{dT} = \frac{L_f}{RT^2}$$

If this is integrated between T and T_o (where $X_1 = 1$)

$$\ln X_1 = \frac{L_f}{R} \left(\frac{1}{T} - \frac{1}{T_o} \right)$$

where T is the freezing point of the solution at solvent concentration X_1 . This assumes that L_f is independent of temperature, which is not strictly true, but this approximation was used, since the normal variation of L_f with temperature would increase the freezing point depression in contrast to the real nonideality of the solutions, which tends to decrease the depression.

Using the last equation, the freezing point, T , was calculated for various concentrations of F_2 in OF_2 and OF_2 in F_2 . A value of 122 cal/mole was used for the heat of fusion of F_2 (Reference 5). No value for the heat of fusion of OF_2 could be found in the literature, so it was estimated that the entropy of fusion was 6.5, which implies a heat fusion of 320 cal/mole. This value was used for the calculations

involved for constructing the phase diagram. A minimum freezing temperature of 39°K at an F_2 mole fraction of 0.65 resulted.

Solid fluorine is reported to undergo a transition at 45.55°K with a heat of transition of 173.9 cal/mole (Reference 5). Inasmuch as the solid fluorine can exist in two forms above the predicted eutectic temperature, the equilibrium diagram becomes more complicated. The theoretical phase diagram was recalculated using a value of 122 cal/mole as the heat of fusion of fluorine until the transition temperature was reached, after which the liquidus curve was assumed to undergo a change in slope corresponding to the heat of fusion plus the heat of transition. This curve was continued to meet the OF_2 -rich liquidus curve leading to a theoretical minimum freezing point of 40°K at 0.54 mole fraction F_2 .

APPARATUS

A Pyrex apparatus was designed and built for this experiment. It is illustrated in Figures 1 and 2. It consists of a central volume for the test chamber, fitted with inlet tubing, a solenoid operated stirrer, and a thermowell. The central tube is surrounded by several annuli arranged concentrically in the following order -- an annulus in which the pressure can be controlled to control heat transfer rates, an annulus for liquid helium to cool the fluids in test, an evacuated annulus, an annulus for liquid nitrogen (heat shield) and another evacuated annulus. The evacuated annuli were silvered except for strips for observation of the interior.

Liquid helium is supplied to the cooling bath from 25 liter transport Dewars connected to the apparatus by insulated lines. Liquid nitrogen was poured into the heat shield when needed.

Temperatures were measured with a copper-constantan thermocouple inserted in the thermowell with an external reference junction at liquid nitrogen temperature. Thermoelectric potentials were measured with a Grey type E-3067 potentiometer and temperatures estimated from the tables and data of Powell, Bunch, and Corruccini (Reference 6). The thermocouple calibration was checked against boiling liquid nitrogen and hydrogen as fixed points. At 50°K the thermoelectric emf for copper-constantan is about 12.1 microvolts per degree. With a sensitivity of 5 microvolts or better for the potentiometer, the sensitivity of temperature reading is about 0.4°.

MATERIALS

The oxidizers tested were obtained in the gaseous state from commercial suppliers. Fluorine supplied by Air Products and Chemicals was passed over an NaF absorption scrubber to reduce the HF content to 0.02 vol %. Oxygen difluoride supplied by Allied Chemical Division of General Chemical was also treated with NaF to remove HF.

PROCEDURE

The quantities of fluorine and oxygen difluoride were measured by volume in the liquid state; weights were calculated from reported (References 7 and 8) densities. A glass ampul of calibrated volume was attached to the oxidizer supply manifold. The system was evacuated, the measuring apparatus and the ampul were chilled with LN_2 to 77°K, the test apparatus was valved off, and the oxidizer supply was valved open. When sufficient oxidizer had condensed in the ampul, the supply was shut off, the line to the test unit was valved open, and the LN_2 was removed from around the ampul, causing the oxidizer to distill into the test apparatus. When distillation was complete, the ampul was valved off.

After condensation of oxidizer was complete, the solenoid stirrer was activated, liquid helium was supplied to the cooling bath, and the pressure in the heat-transfer annulus adjusted to attain a cooling rate of about $1^{\circ}\text{K}/\text{minute}$. The emf of the thermocouple was continuously monitored, and the value recorded at 30 second intervals. The appearance of the oxidizer was observed visually during the experiment.

The experiments were conducted with F_2 , with OF_2 , and with several mixtures of F_2 and OF_2 . The recorded thermocouple potentials were converted to temperatures from which cooling curve graphs (temperature vs. time) were plotted for each solution concentration. Figure 3 is a typical example. Temperatures at which breaks in the curves occurred were identified, and these were plotted on a temperature vs. concentration graph to provide a typical phase diagram (Figure 4). The data used for plotting the phase diagram are tabulated in Table I.

RESULTS AND DISCUSSION

It was determined that, within the accuracy of the experiments, the binary system $\text{F}_2\text{-OF}_2$ exhibited typical eutectic formation with a probable break in the fluorine-rich liquidus curve due to a solid phase transition at $45 \pm 0.5^{\circ}\text{K}$. The accuracy of the temperature measurements was $\pm 0.5^{\circ}\text{K}$. When the temperature-composition curves were plotted and extrapolated to their intersection (the eutectic), the error in composition was ± 2 mole %. This variation is indicated on the graphs by the bars through the experimental points. The errors in quantities of components used are believed to be considerably less than these. The eutectic temperature is estimated to be $43 \pm 0.5^{\circ}\text{K}$ and the eutectic composition 0.59 ± 0.02 mole fraction fluorine.

TABLE I
OBSERVED FREEZING POINTS -- $\text{OF}_2\text{-F}_2$ MIXTURES

	Mole % F_2	Initial F. P. $^{\circ}\text{K}$	Transition Temp. $^{\circ}\text{K}$	Eutectic F. P. $^{\circ}\text{K}$
1.	100.0	53.0	-	-
2.	80.0	48.3	45.0	43.5
3.	69.5	-	45.0	42.4
4.	46.0	45.6	-	43.3
5.	28.0	47.8	-	43.4
6.	0	49.2	-	-

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GLOSSARY

P = vapor pressure
L = latent heat
R = gas constant
T = temperature, $^{\circ}\text{K}$

SUBSCRIPTS

s = solid state or solid-gas transition
L = liquid state or liquid-gas transition
e = evaporation
f = fusion
l = solution
o = freezing point of pure solvent

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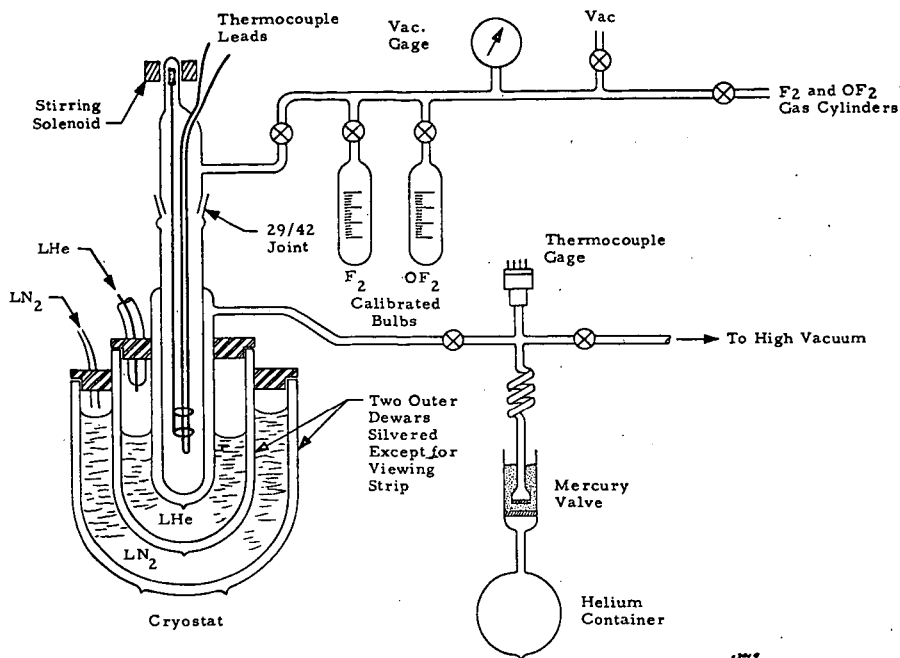


Figure 1. Freezing Point Apparatus

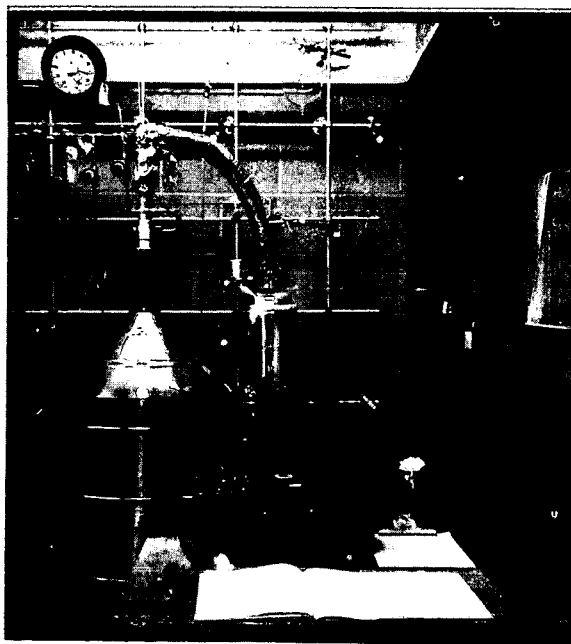


Figure 2. Freezing Point Apparatus

